Scientific Annals, School of Geology, Aristotle University of Thessaloniki Proceedings of the XIX CBGA Congress, Thessaloniki, Greece	Special volume 100	31-38	Thessaloniki 2010

ON THE MINERALOGY, PHYSICAL CHARACTERISTICS AND THE MAIN ELEMENTAL CONTENT OF URBAN ROAD DUST PARTICLES FROM THE HISTORIC CENTRE OF THE CITY OF THESSALONIKI, NORTHERN GREECE

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Abstract: The objective of this study was to characterize urban road dust particles and to study their possible health effects. Road re-suspended dust has been recognized as one of the major contributors to TSP elevating concentrations in Thessaloniki. Eight samples of road dust were collected from the accumulated matter at the edges of major roads in the historic centre of the city of Thessaloniki. The predominant size fraction, according to mass, was 125–500μm, while the mass fraction of the suspendable dust particles (20-63μm and <20μm) was the lowest. Special emphasis was given to the mineralogical characteristics of the urban deposits. Road dusts were mainly composed of quartz, calcite, while plagioclase, dolomite, K-feldspars, amphiboles, micas and chlorite were contained in minor amounts. Amorphous phase was also determined mainly in the finer fractions (20-63μm and <20μm). Scanning electron microscopy shows that dust particles consist of subhedral to anhedral crystalline grains, near-spherical and irregular agglomerates as well as few organic materials. EDS analyses reveal that the composition of dust particles is basically Ca-rich, Fe-rich and silicates.

Keywords: road dust, mineral content, grain size distribution, morphology

1. Introduction

Solid matter, which is composed of soil, anthropogenic metallic constituents, and natural biogenic materials, is called dust. The particles of dust that deposit from the atmosphere and accumulate along roadsides are called road dust particles. Two main sources of road dust are deposition of previously suspended particles (atmospheric aerosols) and displaced soil (Ferreira-Baptista and DeMiguel, 2005). Additionally, the emissions from vehicular traffic, heating systems, building deterioration, construction and renovation, corrosion of galvanized metal structures etc. contribute directly to the road dust load (Howari et al., 2004; Al-Khashman, 2004).

Road dust consisting primarily of mineral matter dominates the total suspended particulate mass (Pakkanen et al., 2001). Apart from the discomfort caused by the dust, respirable mineral particles, e.g. aluminosilicates and crystalline quartz have been implicated in human disease with lung cancer as most severe (Puledda et al., 1999; Powell, 2002). Whether these effects are significant in urban conditions is still unknown. Studies of exposure to mineral and resuspension particles have shown evidence of toxicity and a possibility of adverse health effects (Tiittanen et al., 1999; Salonen et al., 2000).

Furthermore, physical and chemical nature of road dust particles are critical to estimating their potential contributions to environmental and health effects (Brookman and Drehmel, 1981). The physical aspect is basically particle size and shape, while the chemical aspect relates to dust particles composition.

Suspendability of road dust is of paramount importance since this is the principal aspect that relates to human health. The quantity of material suspended depends primarily on particle size (Pye, 1987; Han et al., 2003). Particle size also affects the amount that remains suspended to become part of the TSP (Total Suspended Particles) background and the amount that falls out of the atmosphere within a short distance from the roadway. Dust particles greater than 500 μm are too large to enter the wind stream and move along the surface during wind erosion by surface creep. Medium size particles, 100-500μm in diameter, may enter the wind stream momentarily, but then settle quickly. Only dust particles less than 100μm (most commonly <63μm) are easily entrained and suspended in the wind stream where they are transported, often for great distances.

The chemical nature of the road dust determines whether or not the material is of a hazardous nature to its surroundings (e.g., toxic to man, harmful to vegetation and water supplies). It also helps establish the origins of the dust and can point the direction towards effective controls.

The city of Thessaloniki is the second largest of Greece and one of the largest urban agglomerations in the Balkans. Historically, Thessaloniki has been encountered serious air-quality problems with air particles, with TSP concentrations exceeding by far the annual limit of 150 mg/m^3. Although a 30% reduction has been obtained during the last decade, the excessive use of cars and ongoing works to build a metro system are keeping TSP levels still high, posing a real risk for the health of Thessaloniki residents. Manoli et al. (2002) found that road dust dominated the coarse particle fraction (3.0-10 μm) in the centre of Thessaloniki, accounting for 57% to its ambient levels, while it was also an important contributor (28%) to the fine size fraction (<3.0 μm) where traffic emissions prevailed. A more recent source apportionment study carried out in Thessaloniki (Samara et al., 2003), estimated the contribution of road dust to ambient PM10 at three sites within the city as ranging between 19 and 22%.

The aim of the present study was to assess the mineralogy, particle size, morphology and the main elemental content of urban road dust particles. Similar studies have not been previously conducted in this region. On the contrary, heavy metals and other toxic elements, polycyclic aromatic hydrocarbons and ionic species found in roadside dusts of Thessaloniki have been investigated (Misaelides et al., 1989; Samara et al., 2003; Ewen et al., 2009).

2. Materials and Methods

2.1. Study area

Thessaloniki (40^{o} 62΄ E, 22^{o} 95΄ N) is one of the most densely populated cities in Greece and in Europe accounting for approximately 16,000 inhabitants km^{-2} (Samara et al., 2003). It is located in the inner part of Thermaikos Gulf, surrounded north, north-eastern by Hortiatis mountain (1200 m height). Numerous residential suburbs circle the city and an extended industrial zone is sited north-westerly. According to Manoli et al. (2002), the climate of Thessaloniki is typically Mediterranean: mild, strongly influenced by the sea breeze. Mean monthly values of relative humidity vary between 47% and 80% (mean annual rainfall is 490 mm), while temperature varies between 5.5^{o}C (in January) and 28^{o}C (in August). Prevailing wind directions are N/NW (25%), S/SW (30%) and calms (20%). This meteorology results to insufficient dispersion of atmospheric pollutants.

2.2. Sample Collection and Preparation

Eight samples of road dust were collected from the accumulated matter at the edges of major roads in the historic centre of the city of Thessaloniki (Fig. 1). Road dust sampling was carried out in November 2009. The dust samples were mainly collected by sweeping an area of about 1 m^2 from road surface using a clean plastic dustpan and brushes for each sampling site. The amount of material from each sampling point varied between 50 and 150 g. The samples were dried in an oven at 35^{o}C for 3 days. The dried samples were passed through a 1000μm stainless steel sieve to remove sand-sized materials and large plant roots. Subsequently, the road dust samples were mechanically sieved into five grain size fractions: <20μm, 20-63μm, 63-125μm, 125-500μm, >500μm. The loss of material during sieving was less than 2%. The three finest fractions were used for further investigations.

2.3 Analytical Methods

Mineralogical characterization of the dust particles as well as semi-quantitative mineral determination was performed by X-Ray powder diffraction (XRPD) using a Philips PW1710 diffractometer. Ni-filtered copper Kα radiation was used energized to 35kV and 25mA. Randomly oriented road dust samples of the <20μm, 20-63μm and 63-125μm fractions were scanned continuously from 3 to 63° 2θ angles at a scanning speed of 1.2^{o}/min. The characterization of the mineral phases was performed semi-quantitatively on the basis of the intensity (counts) of specific reflections, the density, and the mass absorption coefficient (CuKα) of the identified mineral phases.

The percentage of total amorphous material

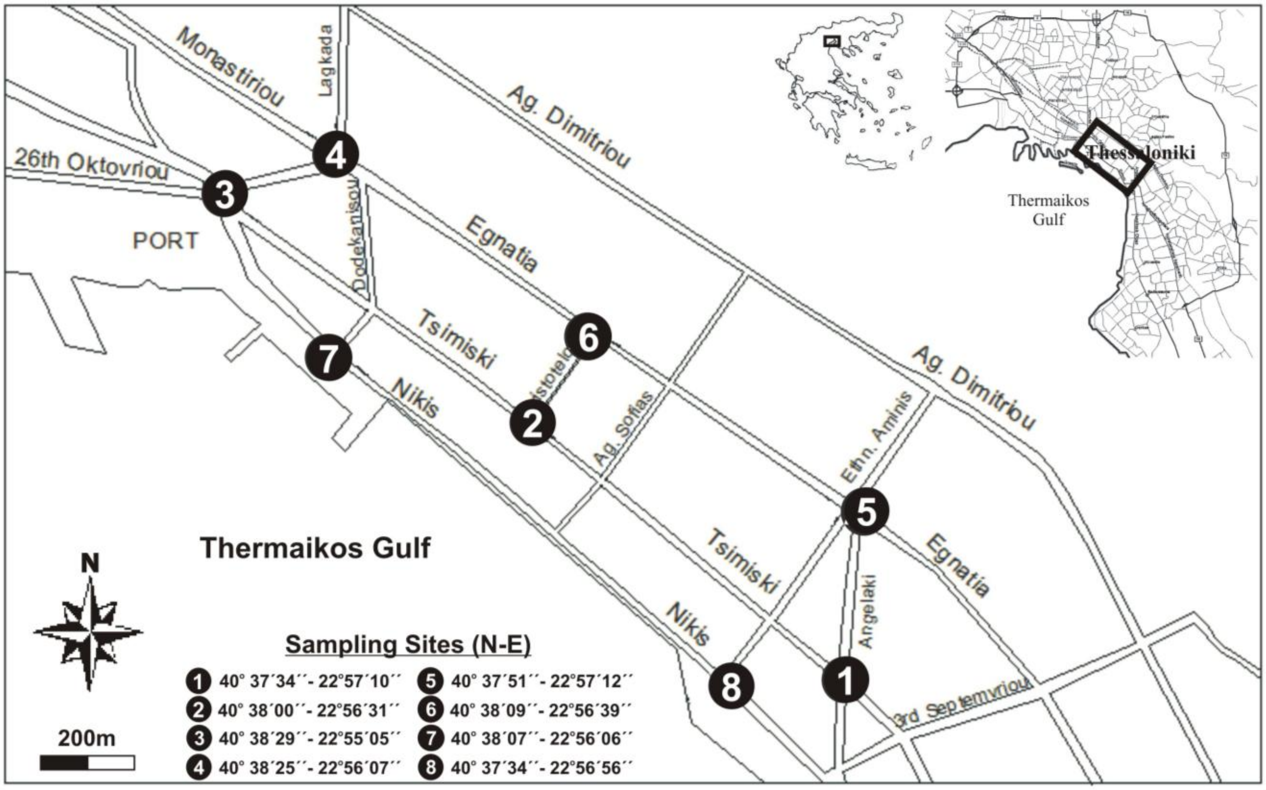

Fig. 1. Location of the sampling sites.

contained in the road dust samples was determined using the methodology described by Kantiranis et al. (2004). The XRPD method is a very good, effective and useful tool for the determination of the percentage of amorphous material contained in a natural or synthetic sample (Kantiranis et al., 2004).

A Scanning Electron Microscope (JEOL JSM-840) connected to an X-ray Energy Dispersion Spectrometer-EDS (LINK-AN 10000) was employed for the morphological and semi-quantitative chemical characterization of the 20-63μm and 63-125μm grain size fractions of the urban road dust samples. This technique allows the definition of the particles with respect to their size and morphology as well as the identification of other properties such as particles association or aggregation (Buseck and Bradley, 1982; Zou and Hooper, 1997).

3. Results and Discussion

3.1. Particle size distribution of road dusts

The grain size distribution of the road dust samples is presented in Figure 2. According to weighted mass, the predominant grain size fraction was 125–500μm varying between 41.9 and 51.8%, while the second most dominant grain size fraction was 63–125μm ranging between 16.6–25.2%. Dust particles which could easily be entrained and suspended in the wind stream were those which had the smallest particle sizes (20-63μm and <20μm). The mass fraction of these suspendable dust particles was the lowest ranging from 7.8-23.2% to 0-0.6%, respectively. This size distribution trend of the road dusts was similar in all sampling sites.

3.2. Mineral Content

The results of the semi-quantitative estimation of the mineralogical composition of the studied road dust samples are summarized in Table 1, while representative XRPD patterns are given in Fig. 3.

The dominant minerals present in the road dust samples were quartz (SiO_2) and calcite ($CaCO_3$). Lower abundances of plagioclase (mostly albite-$NaAlSi_3O_8$) and dolomite ($CaMg(CO_3)_2$) occur in almost all the studied samples. Other minerals identified in small quantities were K-feldspars (mostly orthoclase-$KAlSi_3O_8$), amphiboles (mostly tremolite-$Ca_2Mg_5Si_8O_{22}(OH)_2$), micas (mostly muscovite-$KAl_2(AlSi_3)O_{10}(OH)_2$), and chlorite (mostly clinochlore-$Mg_6Si_4O_{10}(OH)_8$). The prevailing identified minerals were the same in all the studied fractions of the urban road dust samples.
The data available on the mineralogical compositions of urban deposits worldwide, principally based on road dust samples is limited (Kuang et

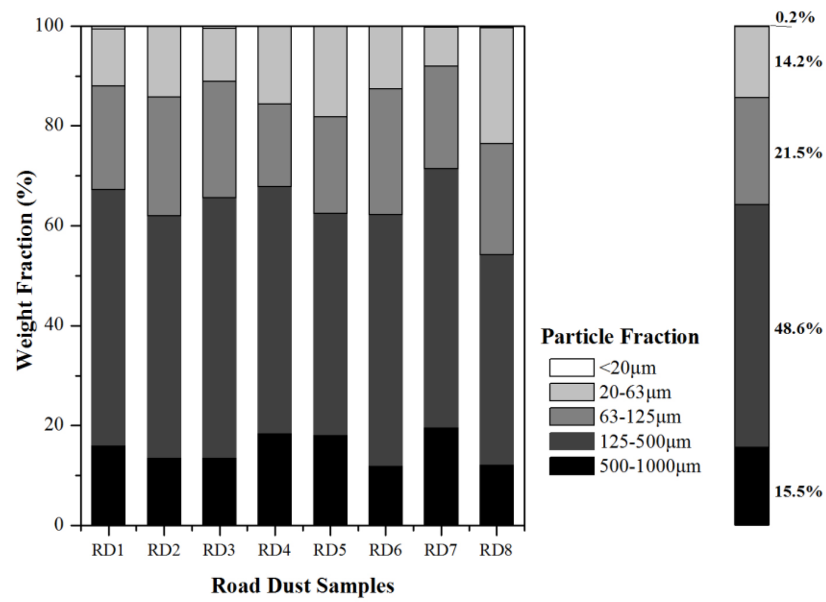

Fig. 2. Grain size distribution (wt%) of the urban road dust samples. The total average value (wt%) of each particle fraction is shown at the right.

al., 2004, Duzgoren-Aydin et al., 2006). Despite a significant variation in the level of contamination and the differences in urban natural and anthropogenic settings, the major mineral components of the road dusts appear to be similar, and are dominated by quartz, calcite and feldspar minerals (including plagioclase and K-feldspars). Quartz, the most resistant mineral to physical and chemical weathering, dominates the overall mineralogy of the urban deposits. Calcite, one of the most abundant minerals in the road dusts, derives probably from the erosion of concrete pavements and other construction materials (Tossavainen and Forssberg, 1999).

The amount of quartz decreases with decreasing particle size (Tab.1). The quartz percentage varies

Table 1. Semi-quantitative mineralogical composition (mass/mass, %) of separated particle size fractions (in μm) of urban road dusts from Thessaloniki city.

Sample	Particle Size	Q	C	Pl	D	Kf	Amp	M	Chl	Amorphous
RD1	63-125μm	78	16	2	2			2		
	20-63μm	47	19	4	3	1		1		25
	<20μm	20	44	1	3	3				29
RD2	63-125μm	83	11	3	1	1		1		
	20-63μm	69	23	5	1		1	tr	tr	
RD3	63-125μm	77	13	1	7	tr	tr	1	tr	
	20-63μm	46	25	2	8				tr	19
	<20μm	18	52	1	6		1			22
RD4	63-125μm	62	19	13	tr		1	1	tr	3
	20-63μm	49	25	4	1	1	1			19
RD5	63-125μm	64	29	4	tr			2	tr	
	20-63μm	27	55	9	tr	tr		tr	tr	8
	<20μm	13	51	1	tr					35
RD6	63-125μm	64	10	2		1	1	tr		21
	20-63μm	80	18	2						
RD7	63-125μm	64	25	5	3		1	1	tr	
	20-63μm	60	29	3	3			1	tr	4
	<20μm	26	43	1	4		tr			25
RD8	63-125μm	77	16	4	2			1		
	20-63μm	64	29	4	2	tr		tr	tr	
	<20μm	29	35	2	2					32

Q: quartz, C: calcite, Pl: plagioclase, D: dolomite, Kf: K-feldspars, Amp: amphibole, M: mica, Chl: chlorite, tr: traces

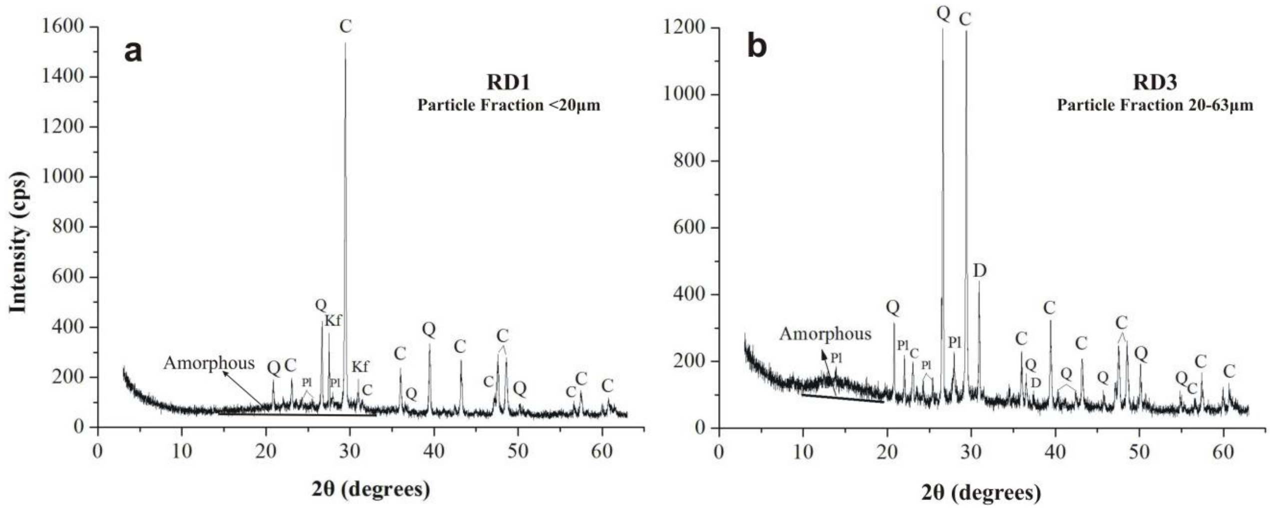

Fig. 3. Representative XRPD patterns of suspendable particle size fractions of road dust samples, a) RD1 and b) RD3. Q: quartz, C: calcite, D: dolomite, Pl: plagioclase, D: dolomite, Kf: K-feldspars.

from 62-84% and 26-80% in the 63-125μm and 20-63μm, respectively. Lower abundances (13-30%) occur in the finer fraction (<20μm). The opposite trend is noticed for calcite. The calcite amount increases with decreasing particle size. In the 63-125μm fraction the calcite percentage varies from 11-29%, while in the finer fraction calcite ranged from 36-56%. This fact is correlated with their erodibility.

The potential health risks associated with crystalline silica are of enhanced interest (Ikeda et al., 1986, Puledda et al., 1999). The latest monograph that the International Agency for Research on Cancer (IARC) devoted to crystalline silica establishes that exposure to this substance can be associated to lung cancer. On this basis, IARC has classified crystalline silica as carcinogenic to man (Category I) (IARC, 1997). By reference to its physical characteristics, there is great concern about the potential health risks resulting from exposure to quartz, the most common mineral phase of crystalline silica. In the present work, relatively high quartz amounts (13-80%) were determined in the suspendable fractions (20-63μm and <20μm) of the road dust samples. However, these results do not permit an assessment of the actual risk for the general population. Health risk depends largely on quartz morphology.

Finally, amorphous phase was also determined. The amorphous phase was mainly in the finer fractions (20-63μm and <20μm). In the <20μm fraction, the amorphous ranged from 19-35%, while in the 20-63μm fraction varied between 4-25%. Only two samples, RD4 and RD6, presented amorphous phase in the 63-125μm fraction. The amorphous phase could probably consist of amorphous silica or Fe-Mn oxyhydroxides which can be found in road dust samples and present poorly crystallized nature.

3.3. Morphology and Chemical Composition

SEM can provide size and morphology information of particles. SEM observation showed that dust particles were present in a wide range of size and shape. Depending on the origin of dusts, the dust particles mostly consist of subhedral to anhedral crystalline grains, plate like and near-spherical particles, and finally irregular agglomerates that contain variable size and amount of particles. The EDS results reveal that the composition of dusts is dominated by Ca-rich or Fe-rich particles and silicates.

Road dusts particles are mainly composed of silicates presenting angular and irregular shapes, which is characteristic of natural sources. Si-rich particles of road dusts are shown in Fig.4. Most of the Si-rich particles contain Si, Al, Fe, and Mg. Si-rich particles are mainly composed of amorphous or crystalline silicate minerals, while Si-rich particles with high iron content are mainly derive from building sites.

Electron micrographs of Ca-rich particles are shown in Figure 5. Ca-dominant particles are mainly composed of $CaCO_3$ (Fig. 5a). The size of Ca-rich particles is typically 10–70μm. Agglomerates of Ca-rich particles are composed of calcium with traces of Si, Al, Mg, K and S (Fig. 5b-c). Additionally, agglomerates of Ca-aluminosilicates are

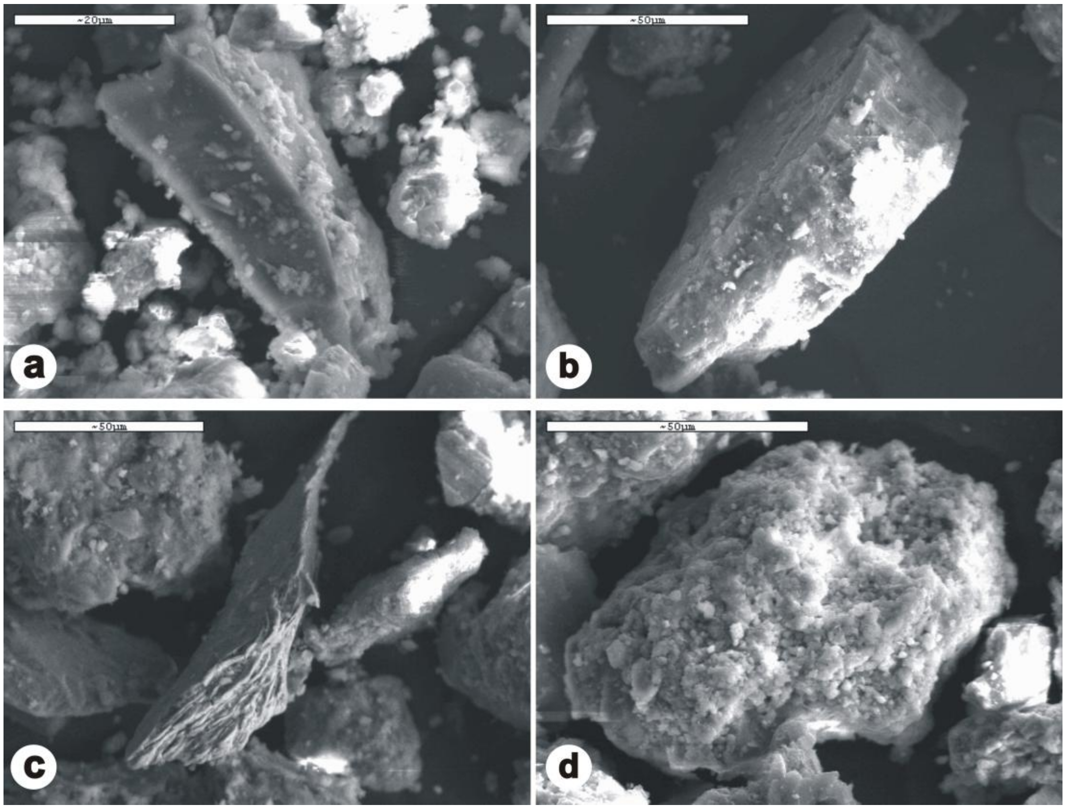

Figure 4: SEM images of Si-rich particles, a) irregular quartz crystal, b) oblate particle of alumino-silicate , c) plate like mica crystal and d) agglomerate of Si-rich particles.

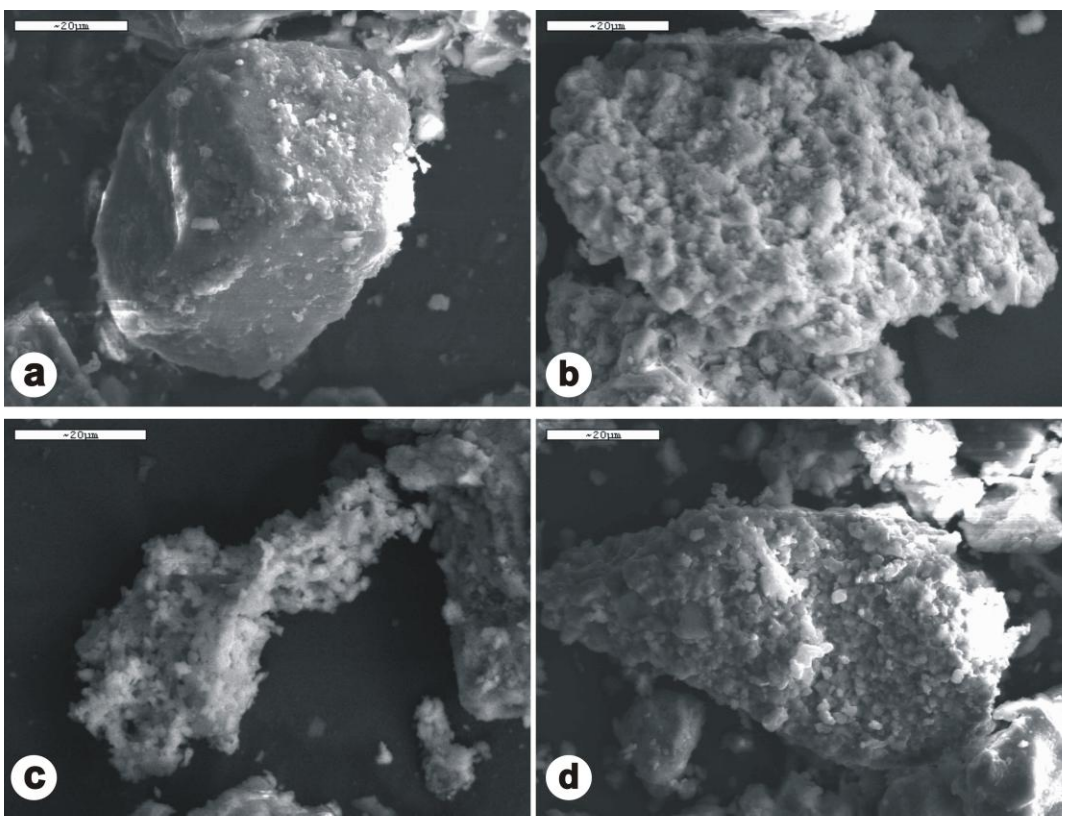

Fig. 5. SEM images of Ca-rich particles. a) calcite crystal, b) agglomerate of Ca-rich particles, c) spongy like agglomerate of Ca-rich particles and d) agglomerate of Ca- and Si-rich particles.

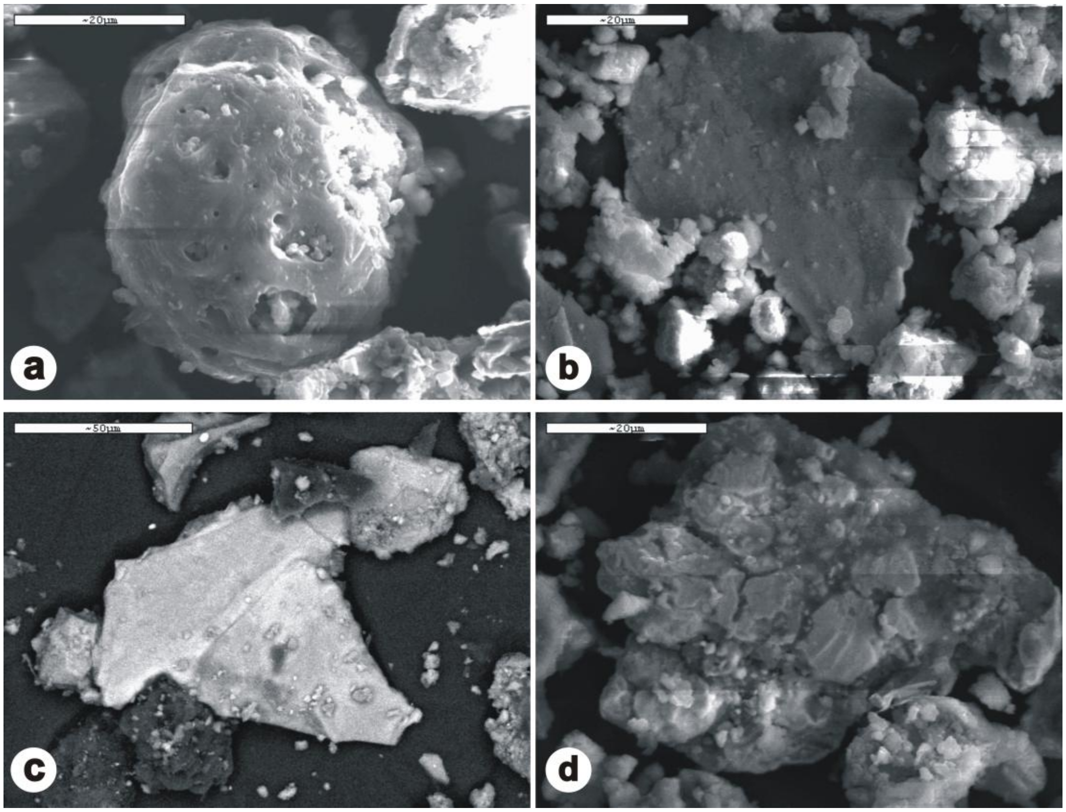

Fig. 6. SEM images of Fe-rich road dust particles, a) near spherical Fe-rich particle, b) plate like and c) irregular plate like Fe-rich particle and d) agglomerate of Fe-rich particles.

determined. The chemical composition of these particles is mainly Si and Ca with minor S, Mg, Fe, Al and K. Ca+Si particles are believed to be a mixture of $CaCO_3$ with silicates (Fig. 5d). Ca-rich particles derive from the erosion of concrete pavements and other construction materials. Sulphur, which produced during fuel combustion is seen as a coating on the surface of Ca-rich dust particles and/or as gypsum from the degradation of the building mortars. As indicated sulfur content in these particles has a range of 0.43–3.13%.

Fe-rich particles are mainly in shapes of near-sphere, plate and agglomerate (Fig. 6). The Fe-rich near-spherical grains exhibit smooth textures (Fig. 6a). The chemical compositions of particles determined by EDS shows that the spherical grains have very high iron content (~70%) with small amounts of Ca and Si. The size of plate Fe-rich particles is typically 10–50μm (Fig. 6b-c). Plate Fe-rich particles contain traces of Si, Al, Ca, Mg, Ti, S and Cr. These non-spherical Fe-rich particles are suggested to be released from vehicles via exhaust emission and the abrasion or corrosion of the vehicle engine and body work (Hoffmann et al., 1999). Agglomerate of Fe-rich particles exhibits cluster texture (Fig.6d).

4. Conclusions

A mineralogical, morphological and chemical characterization of road dust from the historic centre of the city of Thessaloniki was performed. The prevailing identified minerals were quartz and calcite. Numerous studies in literature deal with the potential health risks that could be associated with the occupational exposure to quartz. Additionally, Ca-bearing minerals (e.g. calcite), which are among the most common minerals in the urban environment are strongly linked to certain contaminants (such as Pb and Zn) known to be strongly associated with the operationally defined carbonate fraction. The road dust particles, which are variable in morphology and chemical composition, are mainly composed of near-spherical, plate and irregular agglomerate Fe-rich particles, Ca-rich, and silicate particles. Some of the dusts in the present investigation were rich in potential toxic heavy metal elements (e.g. Cr), which are significant environmental issues. Road dust is often considered only as a nuisance or minor safety hazard. However, environmental consequences in terms of air and water pollution and associated health hazards, primarily those linked to respiratory diseases, render essential further investigation regarding the problem of urban road dust.

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